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LITHIUM CELL WITH IMPROVED CATHODE

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Lithium CELL WITH IMPROVED CATHODE

FIELD OF THE INVENTION

This invention relates to a lithium electrochemical cell with a cathode comprising copper vanadates selected from CuV_2O_6 or $Cu_2V_2O_7$, and mixtures thereof.

BACKGROUND OF THE INVENTION

Electrochemical cells commonly contain a negative electrode (anode) and a positive electrode (cathode), an electrolyte permeable separator therebetween and an electrolyte in contact with both of the electrodes. Electrolytes can be aqueous-based or non-aqueous organic solvent-based liquid electrolytes or polymeric electrolytes. There are two basic types of electrochemical cells, a primary (nonrechargeable) and a secondary (rechargeable) cell. A primary electrochemical cell is discharged to exhaustion only once. A secondary electrochemical cell, however, is rechargeable and thus can be discharged and recharged multiple times.

Primary (non-rechargeable) lithium cells have an anode comprising lithium and a cathode comprising manganese dioxide, and electrolyte comprising a lithium salt such as lithium trifluoromethane sulfonate ($LiCF_3SO_3$) dissolved in a mixtures of nonaqueous solvents. These lithium cells (Li/MnO_2 cells) are commonly in the form of button (coin shaped) cells, prismatic or polyhedral cells (wherein one or more of the housing surfaces are flat, typically of cuboid, namely, rectangular parallelepiped shape) or cylindrical cells, e.g. 2/3 A cell

having about 2/3 the height of conventional AA alkaline cells. (The 2/3 A cell has an IEC designation "CR17335" and has a diameter of about 15 mm and height of about 32 mm). The Li/MnO_2 cells have a voltage of about 3.0 volts which is twice that of conventional Zn/MnO_2 alkaline cells and also have a higher energy density (watt-hours per cubic centimeter of cell volume) than that of alkaline cells. (Alkaline cells as referenced herein shall be understood to be conventional commercial alkaline cells having an anode comprising zinc, a cathode comprising manganese dioxide, and an electrolyte comprising aqueous potassium hydroxide.) Therefore, Li/MnO_2 cells can be used in compact electronic equipment, especially photographic cameras, which require operation at higher voltage and at higher power demand than individual alkaline cells.

Primary lithium electrochemical cells typically employ an anode of lithium metal or lithium alloy, preferably a lithium-aluminum alloy; a cathode containing an electrochemically active material consisting of a transition metal oxide, preferably manganese dioxide; and an electrolyte containing a chemically stable lithium salt dissolved in an organic solvent or a mixture of organic solvents. (The term "anode active material" or "cathode active material" as used herein shall be understood to mean material in the anode or cathode, respectively, which undergoes useful electrochemical reaction during cell discharge, contributing to the cell's capacity and voltage.)

The lithium anode is preferably formed from a sheet or foil of lithium metal or lithium alloy without any substrate or lithium metal deposited or coated on a metallic substrate such as copper or other metals. A lithium primary cell referenced hereinafter as having an anode comprising "lithium" shall be understood to mean an anode of lithium metal or a lithium alloy.

If a lithium-aluminum alloy is employed, the aluminum is present in a very small amount, typically less than about 1 wt% of the alloy. The addition of aluminum primarily serves to improve the low temperature performance of the lithium anode in lithium primary cells.

Manganese dioxides suitable for use in lithium primary cells include both chemically produced manganese dioxide known as "chemical manganese dioxide" or "CMD" and electrochemically produced manganese dioxide known as "electrolytic manganese dioxide" or "EMD". CMD can be produced economically and in high purity, for example, by the methods described by Welsh et al. in U.S. Patent No. 2,956,860. However, CMD typically does not exhibit energy or power densities in lithium cells comparable to those of EMD. Typically, EMD is manufactured commercially by the direct electrolysis of a bath containing manganese sulfate dissolved in a sulfuric acid solution. Processes for the manufacture of EMD and representative properties are described in "Batteries", edited by Karl V. Kordesch, Marcel Dekker, Inc., New York, Vol. 1, 1974, pp.433-488. Manganese dioxide produced by electrodeposition typically is a high purity, high density, "gamma(γ)-MnO_2" phase, which has a complex crystal structure containing irregular intergrowths of a "ramsdellite"-type MnO_2 phase and a smaller portion of a beta(β)- or "pyrolusite"-type MnO_2 phase as described by deWolfe (Acta Crystallographica, **12**, 1959, pp.341-345). The gamma(γ)-MnO_2 structure is discussed in more detail by Burns and Burns (e.g., in "Structural Relationships Between the Manganese (IV) Oxides", Manganese Dioxide Symposium, **1**, The Electrochemical Society, Cleveland, 1975, pp. 306-327).

Electrochemical manganese dioxide (EMD) is the preferred manganese dioxide for use in primary lithium cells. However, before it can be used, it must be heat-treated to remove residual water. The term "residual water", as used herein includes surface-adsorbed water, noncrystalline water (i.e., water physisorbed or occluded in pores), as well as lattice water. Heat-treatment of EMD prior to its use in lithium cells is well known and has been described by Ikeda et al. (e.g., in "Manganese Dioxide as Cathodes for Lithium Batteries", Manganese Dioxide Symposium, Vol. **1**, The Electrochemical Society, Cleveland, 1975, pp. 384-401).

EMD suitable for use in primary lithium cells can be heat-treated at temperatures between about 200 and 350°C as taught by Ikeda et al. in U.S. Patent No. 4,133,856. This reference also discloses that it is preferable to heat-treat the EMD in two steps. The first step is performed at temperatures up to about 250°C in order to drive off surface and non-crystalline water. The EMD is heated in a second step to a temperature between about 250 and 350°C to remove the lattice water. This two-step heat-treatment process improves the discharge performance of primary lithium cells, primarily because surface, non-crystalline, and lattice water are all removed. An undesirable consequence of this heat=treatment process is that EMD having the γ-MnO_2-type structure, is gradually converted to EMD having a gamma/beta (γ/β)-MnO_2-type structure. The term "gamma/beta-MnO_2" as used in the art reflects the fact (as described by Ikeda et al.) that a significant portion of the γ-MnO_2 (specifically, the ramsdellite-type MnO_2 phase) is converted to β-MnO_2 phase during heat-treatment. At least about 30 percent by weight and typically between about 60 and 90 percent by weight of the ramsdellite-

type MnO_2 phase is converted to β-MnO_2 during conventional heat treatment of γ-MnO_2 as taught, for example, in U.S. Patent No. 4,921,689. The resulting γ/β-MnO_2 phase is less electrochemically active than an EMD in which the γ-MnO_2 phase contains a higher fraction of ramsdellite-type MnO_2 relative to β-MnO_2. Thackeray et al. have disclosed in U.S. Patent No. 5,658,693 that cathodes containing such β-MnO_2-enriched phases exhibit less capacity for lithium uptake during discharge in lithium cells.

One consequence of the electrodeposition process used to prepare EMD is that the formed EMD typically contains "residual surface acidity" from the sulfuric acid of the electrolytic bath. This "residual surface acidity" must be neutralized, for example, with basic aqueous solution, before the EMD can be used in cathodes for primary lithium cells. Suitable aqueous bases include: sodium hydroxide, ammonium hydroxide (i.e., aqueous ammonia), calcium hydroxide, magnesium hydroxide, potassium hydroxide, lithium hydroxide, and combinations thereof. Typically, commercial EMD is neutralized with a strong base such as sodium hydroxide because it is highly effective and economical.

An undesirable consequence of the acid neutralization process is that alkali metal cations can be introduced into ion-exchangeable sites on the surface of the EMD particles. For example, when sodium hydroxide is used for acid neutralization, sodium cations can be trapped in the surface sites. This is especially undesirable for EMD used in cathodes of primary lithium cells because during cell discharge the sodium cations can be released into the electrolyte, deposit onto the lithium anode, and degrade the lithium passivating layer. Further, the

deposited sodium cations can be reduced to sodium metal, react with the organic electrolyte solvents, and generate gas, thereby substantially decreasing the storage life of the cells.

A process for converting commercial grade EMD that has been neutralized with sodium hydroxide to the lithium neutralized form is disclosed by Capparella et al. in U.S. Patent No. 5,698,176 and related Divisional U.S. Patent No. 5,863,675. The disclosed process includes the steps of: (a) mixing sodium hydroxide neutralized EMD with an aqueous acid solution to exchange the sodium cations with hydrogen ions and produce an intermediate with reduced sodium content; (b) treating the intermediate with lithium hydroxide or another basic lithium salt to exchange the hydrogen ions with lithium cations; (c) heat-treating the lithium ion-exchanged EMD at a temperature of at least about 350°C to remove residual water.

A method for preparing a lithiated manganese dioxide and its use in primary lithium cells as cathode active material in primary lithium cells is described in U.S. patent 6,190,800 (Iltchev) herein incorporated by reference. The lithiated manganese dioxide recited in this reference is a heat treated lithiated manganese dioxide product having the formula $Li_yMnO_{2-\delta}$, wherein $0.075 \leq y \leq 0.175$ and $0.01 \leq \delta \leq 0.06$, and a predominantly gamma(γ)-MnO_2-type crystal structure.

Thus, as evidenced by the cited prior art, the methods used to prepare active cathode materials comprising manganese dioxide or lithiated manganese dioxide suitable for cathodes in a primary lithium cells require additional refinement in order to substantially improve performance of the lithium cells incorporating such active cathode materials.

SUMMARY OF THE INVENTION

A principal aspect of the invention is directed to a primary (nonrechargeable) lithium cell having an anode comprising lithium, a non-aqueous electrolyte, and a cathode comprising a copper vanadate of formula CuV_2O_6 or $Cu_2V_2O_7$ as cathode active material. The CuV_2O_6 or $Cu_2V_2O_7$ can be used as cathode active material alone or in any admixture thereof. The CuV_2O_6 can be used in admixture with MnO_2 in any mixture thereof to form the cathode active material for the lithium cell. It shall be understood that a portion of the MnO_2 in this case can be in the form of a manganese dioxide such as lithiated manganese dioxide or all of the MnO_2 can be in the form of a lithiated manganese dioxide. The MnO_2 is preferably heat treated to remove residual water. (The term "a manganese dioxide" shall be understood to include MnO_2 and lithiated manganese dioxide.) The lithiated manganese dioxide, for example, as referenced above and hereinafter can have the formula $Li_yMnO_{2-\delta}$, wherein $0.075 \leq y \leq 0.175$ and $0.01 \leq \delta \leq 0.06$ recited in U.S. patent 6,190,800. Alternatively, the $Cu_2V_2O_7$ if employed as cathode active material can be used in admixture with MnO_2 in any mixture thereof to form the cathode active material for the lithium cell. In such case it shall be understood that a portion of the MnO_2 or all of the MnO_2 present in the cathode can be in the form of a lithiated manganese dioxide, for example, a lithiated manganese dioxide having the formula $Li_yMnO_{2-\delta}$, wherein $0.075 \leq y \leq 0.175$ and $0.01 \leq \delta \leq 0.06$ as recited in U.S. patent 6,190,800.

Also, the cathode active material for the lithium cell can comprise mixtures of CuV_2O_6, $Cu_2V_2O_7$, and MnO_2. All or a portion of the MnO_2 in such mixtures can be in the form of a lithiated manganese dioxide. It will be appreciated that the MnO_2 is

desirably heat treated to remove residual water thereby making it more suitable for use as cathode active material in the lithium cell. A conductive carbon, preferably graphite such as natural, or synthetic graphite, preferably expanded graphite, is added to the cathode mixture to improve conductivity.

It has been determined that the primary lithium cell of the invention can comprise a conventional anode, namely, a sheet of lithium or lithium alloy, e.g. lithium-aluminum alloy, preferably, comprising at least 99 percent by weight lithium. (An anode comprising "lithium" as referenced herein shall be understood to mean an anode of lithium metal or such lithium alloy.) The cell may be in the form of a button cell or a spirally wound cell. The electrolyte can be non-aqueous electrolyte, conventionally used in primary lithium cells having a lithium anode and MnO_2 cathode. For example, by way of non-limiting example, the electrolyte can be a lithium salt, such as lithium perchlorate ($LiClO_4$) or lithium trifluoromethylsulfonate ($LiCF_3SO_3$) dissolved in an organic solvent, for example, dimethoxyethane (DME) or, ethylene carbonate (EC) and propylene carbonate (PC). Gel type polymer electrolytes used in conventional lithium-ion rechargeable cells could also be suitable. The separator can be selected from conventional separators for primary lithium cells, for example, the separator can be of microporous polypropylene.

The copper in CuV_2O_6 or $Cu_2V_2O_7$ compound has a +2 valence and the vanadium a +5 valence. The Cu^{+2} and V^{+5} are available for reduction to copper metal and vanadium (V^{+3}) during discharge. On such basis the CuV_2O_6 has a high theoretical specific capacity, namely, 615 milliAmp-hour/g and the $Cu_2V_2O_7$ has a high theoretical capacity of 629 milliAmp-hour/g. This is much

higher than the theoretical specific capacity of MnO_2, which is 308 milliAmp-hour/g. Thus, when CuV_2O_6 or $Cu_2V_2O_7$ compounds are used as cathode active material in a primary lithium cell, this results in higher capacity and also higher total "energy output" when compared to same cell having a MnO_2 cathode.

When CuV_2O_6 or $Cu_2V_2O_7$ are each used alone without any added MnO2, the CuV_2O_6 or $Cu_2V_2O_7$ desirably comprises between about 60 and 95 percent by weight of the total cathode (electrolyte free basis). When CuV_2O_6 and $Cu_2V_2O_7$ are used in admixture without any added MnO2, the mixture of CuV_2O_6 and $Cu_2V_2O_7$ desirably comprises between about 60 and 95 percent by weight of the total cathode (electrolyte free basis), typically between about 60 and 93 percent by weight of the total cathode (electrolyte free basis).

In cathode mixtures of CuV_2O_6 and MnO2 or mixtures of $Cu_2V_2O_7$ and MnO2, the CuV_2O_6 or $Cu_2V_2O_7$ in such mixtures desirably comprises between about 1 and 95 percent by weight of the total cathode (electrolyte free basis), desirably between about 60 and 95 percent by weight of the total cathode (electrolyte free basis). Typically, the CuV_2O_6 or $Cu_2V_2O_7$ in such mixtures comprises between about 60 and 93 percent by weight of the total cathode (electrolyte free basis). In such mixture the MnO_2 may typically comprise between about 10 and 75 percent by weight of the total cathode (electrolyte free basis).

If the cathode comprises both CuV_2O_6 and $Cu_2V_2O_7$ in admixture with manganese dioxide, then the total amount of CuV_2O_6 and $Cu_2V_2O_7$ together is desirably between about 1 and 95 percent by weight of the total cathode (electrolyte free basis), desirably between about 60 and 95 percent by weight of the total cathode (electrolyte free basis). Typically, the amount of CuV_2O_6 and

$Cu_2V_2O_7$ together in such mixtures comprises between about 60 and 93 percent by weight of the total cathode (electrolyte free basis).

BRIEF DESCRIPTION OF THE DRAWING

The figure is a cross sectional view of a typical primary lithium electrochemical button cell.

DETAILED DESCRIPTION

A primary lithium electrochemical cell can be fabricated in the form of a button or coin cell 10 as shown in the figure. The primary lithium cell can also be fabricated in the form of a wound cell, for example, as shown in U.S. 4,707,421, herein incorporated by reference. In the button cell shown in the figure, a disk-shaped cylindrical housing 30 is formed having an open end 32 and a closed end 38. Housing 30 is preferably formed from nickel-plated steel, for example. An electrical insulating member 40, preferably a cylindrical member having a hollow core, is inserted into housing 30 so that the outside surface of insulating member 40 abuts and lines the inside surface of housing 30. Alternatively, the inside surface of housing 30 may be coated with a polymeric material that solidifies into insulator 40 abutting the inside surface of housing 30. Insulator 40 can be formed from a variety of thermally stable insulating materials, for example, nylon or polypropylene. A cathode current collector 15 comprising a metallic grid can be inserted into the cell so that it abuts the inside surface of the closed end 38 of the housing 30. The cathode current collector 15 can be welded onto the inside bottom of the closed end 38 of the housing 30. An optional conductive carbon layer 72 comprising a mixture of graphite and polytetrafluoroethylene (PTFE) binder can be compressed into the

cathode current collector 15 and the cathode material 70 coated onto such conductive layer 72. This may be termed a "staged" cathode construction.

A layer of cathode material 70 of the invention comprising CuV2O6 or Cu2V2O7 or any mixture thereof as active cathode material, may thus be inserted over optional conductive layer 72 overlying cathode current collector 15. The cathode active material in cathode 70 can be composed entirely of CuV2O6. Alternatively, cathode material 70 can comprise mixtures of CuV2O6 and manganese dioxide or mixtures of CuV2O6 and lithiated manganese dioxide as well as mixtures of CuV2O6, manganese dioxide and lithiated manganese dioxide as the cathode active material therein. The lithiated manganese dioxide, for example, can have the form as above referenced in U.S. patent 6,190,800, herein incorporated by reference.

Alternatively, the cathode active material in cathode 70 can be composed entirely of $Cu_2V_2O_7$ or mixtures of CuV_2O_6 and $Cu_2V_2O_7$ with or without an MnO_2 or lithiated MnO_2 added.

In the absence of the conductive layer 72, the layer of cathode material 70 is compressed into cathode current collector 15. A separator sheet 60 is placed overlying cathode layer 70. Nonaqueous electrolyte is added so that it fully penetrates through separator sheet 60 and cathode layer 70. A layer of anode material 50, typically lithium or lithium alloy is placed over separator sheet 60. The anode cover 20, formed preferably from nickel-plated steel, is inserted into open end 32 of housing 30 and peripheral edge 35 of housing 30 is crimped over the exposed insulator edge 42 of insulating member 40. The peripheral edge 35 bites into insulator edge 42 closing housing 30 and tightly sealing the cell contents therein. The anode cover 20 also

functions as the negative terminal of the cell and housing 30 at the closed end 38 functions as the positive terminal of the cell.

Alternatively, a primary lithium cylindrical cell can be fabricated comprising a spirally wound anode and cathode with a separator sheet positioned therebetween. This electrode configuration for primary lithium cells is well known in the art and an embodiment thereof is described in detail, for example, in U.S. 4,707,421. Compositions for the electrodes, separator, and electrolyte as disclosed in U.S. 4,707,421, herein incorporated by reference, can be used for the primary lithium cells of the present invention except that the cathode comprises CuV_2O_6 or $Cu_2V_2O_7$ or mixtures thereof which can include a manganese dioxide added thereto as above referenced.

Synthesis of CuV2O6 and Cu2V2O7

Copper vanadate (CuV_2O_6) was prepared by dry mixing copper oxide (CuO) powder with vanadium pentoxide (V_2O_5) powder in one to one molar ratio. The copper oxide and copper vanadate powders, available from Alfa Aesar Co., each had an average particle size of between about 200 and 300 micron. Vanadium pentoxide was handled with care within a protective environment to prevent direct inhalation. The powder mixture was ball milled in 1 kilogram batches in an electric mixer using zirconia balls as inert milling medium. The powder was mixed in this manner for up to 24 hours to achieve a homogeneous mixture, which was then passed through a sieve to remove the zirconia balls. The filtered mixture was then placed in a ceramic container and heated in a conventional oven at a temperature of about 620° C for about 48 hours in ambient atmosphere. The vanadium pentoxide (V_2O_5) and copper oxide (CuO) powders reacted to form a blue/black powder of single phase crystalline particles having

the formula CuV_2O_6.

The copper vanadate (CuV_2O_6) product synthesized in the above manner had the following properties: The CuV_2O_6 product had a particle size distribution wherein 10% by volume of the product fell below 19.4 micron; 50% by volume fell below 36.6 micron, and 100% by volume fell below 215 micron. The value mean diameter (VMD) which approximates the true mean diameter of the CuV_2O_6 particles was 43.6 micron. The CuV_2O_6 had a BET surface area of about 0.18 m^2/g. The term BET surface area (m^2/g) as used herein shall mean the standard measurement of particulate surface area by gas (nitrogen and/or other gasses) porosimetry as is recognized in the art. The BET surface area measures the total surface area on the exterior of the particle and also that portion of the surface area defined by the open pores within the particle available for gas adsorption and desorption when applied. BET surface area determinations (Brunauer, Emmett and Taylor, method) as reported herein is carried out in accordance with ASTM Standard Test Method D4820-99.

The CuV_2O_6 product had a low solubility of less than 5 parts per million (PPM) in water at room temperature. The CuV_2O_6 product had a measured real density of 4.37 g/cm^3 and a calculated theoretical density of 4.396 g/cm3. The real density of a solid is the solid sample weight divided by real volume. The theoretical capacity of the CuV_2O_6 based on reduction of 6 electrons per molecule (Cu^{+2} to Cu and V^{+5} to V^{+3}) is calculated as 615 mAh/g.

The out of cell gassing was determined for cathodes comprising CuV_2O_6 in admixture with lithium trifluoromethane sulfonate (CF_3SO_3Li) electrolyte. The cathode mixture for the gassing test contained 4.5g CuV_2O_6 and 5 ml electrolyte. The electrolyte comprised a 0.6 M solution of the (CF_3SO_3Li) in an

organic solvent mixture of ethylene carbonate (EC), propylene carbonate (PC), and dimethoxyethane (DME). A comparative cathode mixture comprising manganese dioxide and same electrolyte was prepared and also tested for out of cell gassing. Each mixture was kept in closed chamber at 70° C for five days and the amount of gassing was determined by measuring the internal gas pressure within the chamber. The chamber housing the test cathode comprising CuV_2O_6 and same electrolyte exhibited an increase in internal pressure of about 20 psig. By contrast the chamber housing the comparative cathode mixture of MnO_2 and electrolyte exhibited an increase in internal gas pressure to 45 psig.

Copper vanadate ($Cu_2V_2O_7$) was synthesized in a similar manner using copper oxide (CuO) and vanadium pentoxide (V_2O_5) as starting materials. However, the reaction mixture was prepared by mixing the CuO and V_2O_5 powders in a stoichiometric ratio of 2 moles CuO to one mole V_2O_5. The CuO and V_2O_5 powders each had average particle size of between about 200 and 300 micron as described above. The mixture was blended with an inert media of zirconia balls in an electric mixer for up to 24 hours until a homogenous mixture was achieved. The powder mixture was separated from the inert media and then placed into a ceramic container. The powder mixture in ceramic container was heated in an oven at a final temperature of about 700° C for about 48 hours in ambient atmosphere. At this temperature the CuO and V_2O_5 powders reacted to form a crystalline product having of formula $Cu_2V_2O_7$.

The cathode 70 for the primary lithium cell of the invention consists of a cathode active material mixed with suitable polymeric binders, for example, polytetrafluoroethylene, and conductive agents, for example, carbon black and graphite, to produce a cathode paste or slurry.

The cathode paste can be applied to current collector 15 comprising a highly porous sintered, felted, or foamed electrically-conductive substrate, for example, a stainless steel grid, an expanded metal foam or a metal foil. The cathode active material in cathode 70 can comprise the CuV_2O_6 or $Cu_2V_2O_7$ alone or in any mixtures thereof. Manganese dioxide or lithiated manganese dioxide can be added in any percent by weight as additional cathode active material in admixture with the CuV2O6 or Cu2V2O7 cathode active material. (The manganese dioxide, if included as additional cathode active material is desirably conventional heat-treated manganese dioxide.) Cathode pieces of the appropriate size can be cut from the coated substrate.

The anode 50 comprises anode active material preferably of lithium or a lithium alloy. The anode 50 can be a solid sheet of lithium. The anode 50 is desirably formed of a continuous sheet of lithium metal (99.8 wt.% pure). Alternatively, anode 50 can be an alloy of lithium and an alloy metal, for example, an alloy of lithium and aluminum. An alloying metal, such as aluminum, can be present at a low concentration, typically less than 1 wt.%. Upon cell discharge the lithium in the alloy functions essentially as pure lithium. Thus, the term "lithium or lithium metal" as used herein and in the claims is intended to include such lithium alloy. The lithium sheet, forming anode 50 does not require a substrate. The lithium anode 50 is advantageously formed from an extruded sheet of lithium metal having a thickness of desirably between about 0.15 and 0.20 mm Alternatively, a much thicker lithium metal anode of about 0.75 mm thick could be used for test coin cells, for example, of the type referenced in the examples.

A separator layer 60 is located between the two electrodes.

The separator layer typically consists of a porous polymer film or thin sheet that serves as a spacer and prevents electrical contact between the cathode and anode while allowing electrolyte to move freely through the pores. Suitable separators can include relatively non-reactive polymers such as, for example, microporous polypropylene, polyethylene, a polyamide (i.e., a nylon), a polysulfone, or polyvinyl chloride (PVC). The separator has a preferred thickness between about 10 microns and 200 microns and a more preferred thickness between about 20 microns and 50 microns.

The anode 50, cathode 70 and separator 60 therebetween are contained within housing 30. As described hereinabove, the cell can take the form of a coin cell, button cell, cylindrical cell, prismatic cell, laminar cell or other standard cell geometry. The housing 30 is closed to provide a gas-tight and fluid-tight seal. The housing 30 can be made of a metal such as nickel, nickel clad or plated steel, stainless steel, aluminum or a plastic material such as PVC, polypropylene, a polysulfone, an acrylic acid-butadiene-styrene terpolymer (ABS), or a polyamide. The housing 30 containing the electrodes and separator can be filled with a suitable liquid or a polymeric nonaqueous electrolyte.

The nonaqueous electrolyte can be any nonaqueous electrolyte or combination of nonaqueus electrolytes known in the art. Typically, nonaqueous electrolytes suitable for use in a primary lithium/MnO_2 cell comprise a lithium salt dissolved in an organic solvent or combination of organic solvents. Typically, the salt is lithium perchlorate ($LiClO_4$) or lithium trifluoromethylsulfonate ($LiCF_3SO_3$). Other suitable electrolyte salts include: $LiPF_6$, $LiAsF_6$, $LiBF_4$, lithium

bis(trifluoromethylsulfonyl) imide ($Li(CF_3SO_2)_2N$), and lithium bis(perfluoroethylsulfonyl) imide ($Li(CF_3CF_2SO_2)_2N$). Suitable organic solvents include ethylene carbonate(EC), propylene carbonate(PC), butylene carbonate, and the like; dimethylcarbonate (DMC); diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethoxyethane (DME); dioxolane; gamma(γ)-butyrolactone; diglyme; and mixtures thereof. A preferred electrolyte composition consists of a 0.6 M solution of lithium trifluoromethylsulfonate (CF_3SO_3Li; available under the tradename, FC-122, from 3M) in a mixture of dry ethylene carbonate, propylene carbonate, and dimethoxyethane. Once filled with the nonaqueous electrolyte, the housing 30 is sealed to confine the nonaqueous electrolyte and to inhibit the infiltration of moisture and air into the cell.

The following examples illustrate the invention. Test cells were prepared and balanced so that they were cathode limited, (theoretical capacity of lithium divided by theoretical capacity of total cathode actives above about 1). The cathode theoretical capacity is calculated using the following theoretical specific capacities: Li, 3860 mAh/g; MnO_2, 308 mAh/g; CuV_2O_6, 615 mAh/g; and $Cu_2V_2O_7$, 629 mAh/g.

Example 1 (Comparative - Lithium Anode/MnO2 Cathode)

A button cell 10 is made in accordance with the above description. The button cell 10 was a standard 2430 size having the overall dimensions 24.47 mm diameter and 2.46 mm thickness. The anode material 50 was as above described comprising a sheet of lithium (99.8 wt.% pure). The anode 50 had a weight of ~115 mg. In the test cells slight excess Li weight was used in determining the specific capacity of cathode active material and also to fill up the void volume inside the cells. The separator

60 was of microporous polypropylene membrane of basis weight between about 13.5 and 16.5 g/m^2 and about 0.025 mm thick.

Cathode 70 which was coated onto conductive carbon layer 72 had the following formulation: manganese dioxide (electrolytic manganese dioxide, EMD), 70.0 wt.%, tetrafluoroethylene (Teflon polymer), 3.0 wt.%, conducting carbon additive 27 wt. % (mixtures of Shawinigan carbon black and particulate graphite such as expanded graphite from Timcal Group in different ratios). The manganese dioxide was heat treated in conventional manner to remove residual water (non-crystalline water) therefrom before the cathode coating 70 was prepared. The cathode 70 can be prepared by mixing the above components in a conventional electric blender at room temperature until a homogenous mixture is obtained. The cathode mixture 70 can be coated on one side of the cathode current collector 15. The cathode current collector was a stainless steel expanded metal foil (EXMET stainless steel foil) having a basis weight of about 0.024 g/cm^3. After the anode 50 and cathode 70 is inserted with separator 60 the housing 30 is filled with the above described electrolyte consisting of a 0.6 M solution of lithium trifluoromethylsulfonate (CF_3SO_3Li; available under the tradename, FC-122, from 3M) in a mixture of dry ethylene carbonate, propylene carbonate, and dimethoxyethane. Cell 10 was then sealed as above described.

	Cathode Composition, wt.%
MnO_2	70.0
Tetrafluoroethylene Teflon polymer	3.0
Particulate graphite	27.0
Total	100.0

Fresh cells 10 were discharged at a constant current of 1 milliAmp and 10 milliAmp to a cut off of 1.5 volts. The 1 mA and 10 mA rate in the button cell corresponds to a rate of about 248 mA/g and 171 mA/g, respectively, of the manganese dioxide cathode active material. The cells specific capacity for actives (mAmp-hours/g) and energy output for total cathode actives (mWatt-hours/g), (mWatt-hours/cc) is reported in Table 1 for discharge at 1 milliamp and Table 2 for discharge at 10 milliamp.

Example 2 (Lithium Anode/ CuV2O6 Cathode)

A button cell 10 is made as in Example 1 employing the same size cell, same anode, same electrolyte and components, except that the cathode compositon was changed to employ CuV_2O_6 as cathode active material.

Cathode 70 has the following formulation: CuV_2O_6, 70 wt.%; particulate graphite (expanded graphite from Timcal Group), 27 wt.%; tetrafluoroethylene (Teflon) binder, 3 wt.%. The cathode 70 can be prepared by mixing the above components in a conventional electric blender at room temperature until a homogenous mixture is obtained. The cathode mixture 70 can be coated on one side of the cathode current collector 15. The cathode current collector was a stainless steel expanded metal foil (EXMET stainless steel foil) having a basis weight of about 0.024 g/cm^3. The cathode composition is summarized as follows:

	Cathode Composition, wt.%
CuV_2O_6	70.0
Tetrafluoroethylene Teflon polymer	3.0
Particulate graphite	27.0
Total	100.0

Fresh lithium button cells 10 were prepared having a cathode containing 0.04 gram copper vanadate (CuV_2O_6) and were balanced so that they were cathode limited. The cells were discharged at a constant current of 1 milliAmp and 10 milliAmp to a cut off of 1.5 volts. The 1 mA and 10 mA rate in the button cell corresponds to a rate of about 25 mA/g and 250 mA/g, respectively, of the cathode active material. (Also 1 milliAmp rate in the above button cell using 0.04 gram CuV_2O_6 corresponds to approximately a ~150 milliAmp rate for a 2/3 A cell using about 6 gram of CuV2O6. The 10 milliAmp rate in the above button cell using 0.04 gram CuV_2O_6 corresponds to approximately a ~1500 milliAmp rate for a 2/3 A cell using about 6 gm of CuV_2O_6 actives). The cells specific capacity for actives (mAmp-hours/g) and energy output for total cathode actives (mWatt-hours/g), (mWatt-hours/cc) is reported in Table 1 for discharge at 1 milliamp and Table 2 for discharge at 10 milliamp.

Example 3 (Lithium Anode/ Cu2V2O7 Cathode)

A button cell 10 is made as in Example 1 employing the same size cell, same anode, same electrolyte and components, except that the cathode composition was changed to employ $Cu_2V_2O_7$ as

cathode active material.

Cathode 70 has the following formulation: $Cu_2V_2O_7$, 70 wt.%; particulate graphite (expanded graphite from Timcal Group), 27 wt.%; tetrafluoroethylene (Teflon) binder, 3 wt.%. The cathode 70 can be prepared by mixing the above components in a conventional electric blender at room temperature until a homogenous mixture is obtained. The cathode mixture 70 can be coated on one side of the cathode current collector 15. The cathode current collector was a stainless steel expanded metal foil (EXMET stainless steel foil) having a basis weight of about 0.024 g/cm^3. The cathode composition is summarized as follows:

	Cathode Composition, wt.%
$Cu_2V_2O_7$	70.0
Tetrafluoroethylene Teflon polymer	3.0
Particulate graphite	27.0
Total	100.0

Fresh lithium button cells 10 were prepared having a cathode containing 0.04 gram copper vanadate ($Cu_2V_2O_7$) and were balanced so that they were cathode limited. The cells were discharged at a constant current of 1 milliAmp and 10 milliAmp to a cut off of 1.5 volts. The 1 mA and 10 mA rate in the button cell corresponds to a rate of about 25 mA/g and 250 mA/g, respectively, of the cathode active material. (Also 1 milliAmp rate in the above button cell using 0.04 gram Cu_2V_2O7 corresponds to approximately a ~150 milliAmp rate for a 2/3 A cell using about 6 gram of CuV2O6. The 10 milliAmp rate in the above button cell using 0.04 gram CuV_2O_6 corresponds to approximately a ~1500

milliAmp rate for a 2/3 A cell using about 6 gm of $Cu_2V_2O_6$ actives). The cells specific capacity for actives (mAmp-hours/g) and energy output for total cathode actives (mWatt-hours/g), (mWatt-hours/cc) is reported in Table 1 for discharge at 1 milliamp and Table 2 for discharge at 10 milliamp.

Example 4 (Lithium Anode/ (CuV2O6 + MnO_2 Cathode)

A button cell 10 is made as in Example 1 employing the same size cell, same anode, same electrolyte and components, except that the cathode composition was changed to employ CuV_2O_6 in admixture with MnO_2 as cathode active material.

Cathode 70 has the following formulation: CuV_2O_6, 35 wt.% ; MnO_2, 35 wt.%; particulate graphite (expanded graphite from Timcal Group), 27 wt.%; tetrafluoroethylene (Teflon) binder, 3 wt.%. The MnO_2 was heat treated to remove residual water before use in the cathode. The cathode 70 can be prepared by mixing the above components in a conventional electric blender at room temperature until a homogenous mixture is obtained. The cathode mixture 70 can be coated on one side of the cathode current collector 15. The cathode current collector was a stainless steel expanded metal foil (EXMET stainless steel foil) having a basis weight of about 0.024 g/cm^3. The cathode composition is summarized as follows:

	Cathode Composition, wt.%
CuV_2O_6	35.0
MnO2	35.0
Tetrafluoroethylene Teflon polymer	3.0
Particulate graphite	27.0
Total	100.0

Fresh lithium button cells 10 were prepared having a cathode containing 0.1 gram cathode actives (CuV_2O_6 + MnO2) and were balanced so that they were cathode limited. The cells were discharged at a constant current of 1 milliAmp and 10 milliAmp to a cut off of 1.5 volts. The 1 mA and 10 mA rate in the button cell corresponds to a rate of about 10 mA/g and 100 mA/g, respectively, of the cathode active material. (Also 1 milliAmp rate in the above button cell using 0.1 gram cathode actives (CuV_2O_6 plus MnO_2) corresponds to approximately a ~60 milliAmp rate for a 2/3 A cell using about 6 gram of same composition cathode actives. The 10 milliAmp rate in the above button cell using 0.1 gram cathode actives (CuV_2O_6 plus MnO_2) corresponds to approximately a ~600 milliAmp rate for a 2/3 A cell using about 6 gm of same composition cathode actives). The cells specific capacity for actives (mAmp-hours/g) and energy output for total cathode actives (mWatt-hours/g), (mWatt-hours/cc) is reported in Table 1 for discharge at 1 milliamp and Table 2 for discharge at 10 milliamp.

Example 5 (Lithium Anode/ CuV2O6 + Cu2V2O7 Cathode)

A button cell 10 is made as in Example 1 employing the same

size cell, same anode, same electrolyte and components, except that the cathode composition was changed to employ CuV_2O_6 in admixture with $Cu_2V_2O_7$ as cathode active material.

Cathode 70 has the following formulation: CuV_2O_6, 52.5 wt.%; $Cu_2V_2O_7$, 17.5 wt.%; particulate graphite (expanded graphite from Timcal Group), 27 wt.%; tetrafluoroethylene (Teflon) binder, 3 wt.%. The MnO_2 was heat treated to remove residual water before use in the cathode. The cathode 70 can be prepared by mixing the above components in a conventional electric blender at room temperature until a homogenous mixture is obtained. The cathode mixture 70 can be coated on one side of the cathode current collector 15. The cathode current collector was a stainless steel expanded metal foil (EXMET stainless steel foil) having a basis weight of about 0.024 g/cm^3. The cathode composition is summarized as follows:

	Cathode Composition, wt.%
CuV_2O_6	52.5
$Cu_2V_2O_7$	17.5
Tetrafluoroethylene Teflon polymer	3.0
Particulate graphite	27.0
Total	100.0

resh lithium button cells 10 were prepared having a cathode containing 0.1 gram copper vanadates (CuV_2O_6 plus $Cu_2V_2O_7$) and were balanced so that they were cathode limited. The cells were discharged at a constant current of 1 milliAmp and 10 milliAmp to a cut off of 1.5 volts. The 1 mA and 10 mA rate in the button cell corresponds to a rate of about 10 mA/g and 100 mA/g,

respectively, of the cathode active material. (Also 1 milliAmp rate in the above button cell using 0.1 gram cathode actives (CuV_2O_6 plus $Cu_2V_2O_7$) corresponds to approximately a ~60 milliAmp rate for a 2/3 A cell using about 6 gram of same composition of cathode actives. The 10 milliAmp rate in the above button cell using 0.1 gram cathode actives (CuV_2O_6 plus $Cu_2V_2O_7$) corresponds approximately a ~600 milliAmp rate for a 2/3 A cell using about 6 gm of same composition of cathode actives). The cells specific capacity for actives (mAmp-hours/g) and energy output for total cathode actives (mWatt-hours/g), (mWatt-hours/cc) is reported in Table 1 for discharge at 1 milliamp and Table 2 for discharge at 10 milliamp.

TABLE 1

Fresh Lithium Button Cell With Cathode[1] Comprising CuV_2O_6 or $Cu_2V_2O_7$ (and mixtures) Discharged at 1 mAmp. to 1.5 Volt cut-off at Ambient Temperature

Example[2]	Cathode Actives Weight % of total cathode)	Specific Capacity for Total Cathode Actives (mAh/g)	Energy Out of Total Cathode Actives (mWh/g)	Energy out of Total Cathode Actives, (mWh/cc)
Ex.1 Comparison	MnO_2 (70 wt.%)	248	611	2345
Ex. 2	CuV_2O_6 (70 wt.%)	424	1031	4435
Ex.3	$Cu_2V_2O_7$ (70 wt.%)	388	893	3618
Ex. 4	CuV_2O_6 (35 wt.%); MnO_2 (35 wt.%)	327	695	3161
Ex. 5	CuV_2O_6 (52.5 wt.%); $Cu_2V_2O_7$(17.5 wt.%)	356	713	3021

Notes:

1. The CuV_2O_6 and $Cu_2V_2O_7$ in the above table was synthesized at about 620° C and 700° C, respectively, resulting in a single phase product with desirable microstructure and generally high particle size distribution. The cathodes comprising CuV_2O_6 or $Cu_2V_2O_7$ and mixtures thereof exhibited very little gassing when the cells were discharged.

2. Examples 1, 2 and 3 were based on cells with 0.04 gram of

cathode actives. Examples 4 and 5 were based on cells with 0.1 gram cathode actives.

TABLE 2

Fresh Lithium Button Cell With Cathode[1] Comprising CuV_2O_6 or $Cu_2V_2O_7$ (and mixtures) Discharged at 10 mAmp. to 1.5 Volt cut-off at Ambient Temperature

Example[2]	Cathode Actives Weight % of total cathode)	Specific Capacity for Total Cathode Actives (mAh/g)	Energy Out of Total Cathode Actives (mWh/g)	Energy out of Total Cathode Actives, (mWh/cc)
Ex.1 Comparison	MnO_2 (70 wt.%)	171	380	1823
Ex. 2	CuV_2O_6 (70 wt.%)	385	870	3742
Ex.3	$Cu_2V_2O_7$ (70 wt.%)	358	729	2952
Ex. 4	CuV_2O_6 (35 wt.%); MnO_2 (35 wt.%)	248	545	2485
Ex. 5	CuV_2O_6 (52.5 wt.%); $Cu_2V_2O_7$ (17.5 wt.%)	385	859	3652

Notes:

1. The CuV_2O_6 and $Cu_2V_2O_7$ in the above table was synthesized at about 620° C and 700° C, respectively, resulting in a single phase product with desirable microstructure and generally high particle size distribution. The cathodes comprising CuV_2O_6 or $Cu_2V_2O_7$ and mixtures thereof exhibited very little gassing when the cells were discharged.

2. Examples 1, 2 and 3 were based on cells with 0.04 gram of cathode actives. Examples 4 and 5 were based on cells with 0.1 gram cathode actives.

The test lithium cells employing cathodes comprising CuV_2O_6 or $Cu_2V_2O_7$ or mixtures thereof show generally much higher actual specific capacity (mAmp-hrs/g of total cathode actives) and higher energy output (mWatt-hr per gram or mWatt-hr per cubic centimeter of total cathode actives) than the comparative lithium cells with only MnO_2 actives. This was generally true at both discharge rates employed 1 mAmp (Table 1) or 10 mAmp rate (Table 2) and thus reflects the attractiveness of the CuV_2O_6 and $Cu_2V_2O_7$ vanadates as cathode active material for primary lithium cells.

Although the present invention has been described with reference to specific embodiments, it will be appreciated that variations within the concept of the invention are possible. Thus, the invention is not intended to be limited to the specific embodiments, but rather is defined by the claims and equivalents thereof.